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DERIVATION OF THE BLACKBODY RADIATION SPECTRUM FROM A NATURAL MAXIMUM-ENTROPY PRINCIPLE INVOLVING CASIMIR ENERGIES AND ZERO-POINT RADIATION

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Abstract

By numerical calculation, the Planck spectrum with zero-point radiation is shown to satisfy a natural maximum-entropy principle whereas alternative choices of spectra do not. Specifically, if we consider a set of conducting-walled boxes, each with a partition placed at a different location in the box, so that across the collection of boxes the partitions are uniformly spaced across the volume, then the Planck spectrum corresponds to that spectrum of random radiation (having constant energy $k_B T$ per normal mode at low frequencies and zero-point energy $(1/2)h\omega$ per normal mode at high frequencies) which gives maximum uniformity across the collection of boxes for the radiation energy per box. Our analysis involves Casimir energies and zero-point radiation which do not usually appear in thermodynamic analyses. For simplicity, the analysis is presented for waves in one space dimension.

I. INTRODUCTION

A thermodynamic system described by a known Lagrangian has well-defined restrictions on its adiabatic curves following from the first law of thermodynamics. However, the mechanical Lagrangian does not give the full thermodynamic behavior because it does not determine the thermodynamic entropy. Rather, some additional idea of order, of uniformity, is required for the determination of the entropy function. The assumptions of statistical mechanics regarding equally-probable units provide the idea of uniformity needed to derive the entropy function. Sometimes the idea of uniformity is regarded as immediately evident or natural. For example, in the classical statistical mechanics of particles in a box, it is natural to assume that the situation of maximum uniformity, maximum entropy, corresponds to a uniform spatial distribution for particles in the box. In this article, we propose that there is a similar natural choice for maximum entropy for blackbody radiation in connection with Casimir energies and zero-point radiation; this natural choice leads to the Planck spectrum.

Blackbody radiation is a fundamental thermodynamics system which holds a special place in the history of physics as the beginning point of quantum theory.[1] In the nineteenth century, Boltzmann used Maxwell's connection between radiation pressure and energy density, together with the assumption that the energy density depended upon temperature alone, to derive Stefan's law connecting total energy density and temperature.[2] Wien used adiabatic compression and Maxwell's theory to obtain the displacement law corresponding to the condition on the adiabatic curves for a harmonic oscillator thermodynamic system.[3] However, determination of the full blackbody radiation spectrum seemed to confound classical analysis because no natural entropy analysis seemed possible. Today, the blackbody spectrum is regarded as comprehensible only in terms of energy quanta which are outside of classical theory.

However, in connection with random radiation, twentieth century physics contributed two important ideas, zero-point energy and Casimir forces, which raise new possibilities for recognizing a natural entropy function for thermal radiation. Zero-point energy is random energy which is present even at zero temperature.[4] Thermodynamics allows the possibility of zero-point energy and experimental evidence such as van der Waals forces requires its existence.[5] Casimir forces and energies are those which arise due to the discrete, classical normal modes structure of a system.[6] In total contrast to particles, waves are influenced in the interior of a volume by the presence of boundary conditions at the walls. Thus if a thin conducting partition is introduced into a conducting-walled box, then the energy of the system is changed due to the new boundary conditions at the conducting partition.

Casimir energies serve to couple total electromagnetic radiation energy to the specific spectrum of random radiation. Thus if we consider a collection of conducting-walled containers, each with a partition at a different location, and each box having random radiation at the same temperature, then each of these boxes will have a different (average) thermal energy. And different assumed spectral distributions for thermal radiation will lead to different distributions of energies among the partitioned boxes. Now maximum entropy naturally suggests uniformity. It seems natural to suggest that maximum entropy corresponds to the least variation of energy among the partitioned boxes. We will find that, in the presence of zero-point radiation to prevent an "ultra-violet catastrophe," this natural entropy idea leads to the Planck spectrum for thermal radiation.

II. THERMODYNAMICS OF WAVES IN A ONE-DIMENSIONAL BOX

Although the calculations to be described below can be carried through for electromagnetic waves in a three-dimensional box, we will consider a thermodynamic wave system in one spatial dimension rather than in three because the mathematics is distinctly simpler while the physical ideas are unchanged.[7] Thus we can imagine one-dimensional thermodynamic wave systems consisting of waves on a string, or of electromagnetic waves which are required to move between two conducting walls with wave vectors $\mathbf{k}$ which are always perpendicular to the walls.

Systems satisfying the wave equation in a container with conducting walls can be described in terms of normal modes of oscillation, each of which corresponds to a harmonic oscillator system[8] with Lagrangian

$$L(q_\lambda, \dot{q}_\lambda) = \Sigma_\lambda (1/2)(\dot{q}_\lambda^2 - \omega_n^2 q_\lambda^2) \tag{1}$$

where the q_λ are the amplitudes of the normal modes. For waves in one spatial dimension inside a box of length L, the normal modes can be labeled by a single integer index n where the associated frequency ω_n is given by $\omega_n = cn\pi/L$, $n = 1, 2, 3...$, where c is the speed of the waves. Wien's displacement law, which follows from the application of the laws of thermodynamics to a harmonic oscillator system, tells us that the energy $\mathcal{U}$ of a normal mode at frequency ω and temperature T is given by

$$\mathcal{U}(\omega, T) = -\omega\phi'(\omega/T) \tag{2}$$

where ϕ' is a function of the single variable ω/T.[9]

Wien's displacement law allows two limits which make the energy $\mathcal{U}$ independent of one of its variables. Thus if $\phi' \to const$ when $\omega/T >> 1$, then $\mathcal{U}$ depends upon ω alone. This corresponds to temperature-independent zero-point radiation

$$\mathcal{U} \to \mathcal{U}_{zp}(\omega) = (1/2)\hbar\omega \quad \text{for} \quad \omega/T >> 1 \tag{3}$$

where the constant $\hbar$ must be chosen to have the value of Planck's constant in order to fit with van der Waals forces. On the other hand, if $\phi' \to const/(\omega/T)$, when $\omega/T << 1$, then $\mathcal{U}$ depends upon T alone. This corresponds to the Rayleigh-Jeans spectrum

$$\mathcal{U} \to \mathcal{U}_{RJ}(\omega) = k_B T \quad \text{for} \quad \omega/T << 1 \tag{4}$$

which holds at low frequencies with k_B as Boltzmann's constant.

Since we are not interested in numerical calculations of thermodynamic quantities, we will use natural units[10] where $\hbar = 1$ so that frequency is measured in energy units, and $k_B = 1$ so that temperature is measured in energy units and entropy is a pure number,

$$\mathcal{U}_{zp}(\omega) = (1/2)\omega \quad \text{and} \quad \mathcal{U}_{RJ}(\omega) = T \tag{5}$$

It is convenient to introduce the thermal energy $\mathcal{U}_T(\omega, T)$ of a mode of frequency ω as the mode energy above the zero-point energy

$$\mathcal{U}_T(\omega, T) = \mathcal{U}(\omega, T) - \mathcal{U}_{zp}(\omega) \tag{6}$$

Although the total energy $\mathcal{U}$ is related to forces, only the thermal energy $\mathcal{U}_T$ influences the entropy.[11]

The total thermal radiation energy U_T in a box of length L is given by the sum over the thermal energies $\mathcal{U}_T$ of the modes of frequencies $\omega_n = n\pi c/L$ for integer n. We consider only the thermal energy $\mathcal{U}_T$ since thermodynamics requires that U_T is a finite quantity when summed over all normal modes. In contrast, use of the modes' total energies $\mathcal{U}$ or zero-point energies $\mathcal{U}_{zp}$ will give a divergence in the sum over (infinitely many) high-frequency modes. In a one-dimensional box which is so large that the discrete sum over normal modes can be replaced by an integral, we can use (2) to obtain the total thermal energy $U_T(L,T)$ in the form

$$U_T(L,T) = \Sigma_{n=1}^{\infty}\mathcal{U}_T(\frac{n\pi c}{L},T) = \Sigma_{n=1}^{\infty}\frac{n\pi c}{L}\left[\phi'(\frac{n\pi c}{LT}) - \frac{1}{2}\right]$$

$$\approx \int_0^\infty dn\frac{n\pi c}{L}\left[\phi'(\frac{n\pi c}{LT}) - \frac{1}{2}\right] = \frac{L}{c\pi}T^2\int_0^\infty dzz\left[\phi'(z) - \frac{1}{2}\right] \tag{7}$$

for one space dimension. This is just the Stefan-Boltzmann result appropriate for one space dimension.[12] In the case of waves in three spatial dimensions, the frequencies of the normal modes ω_{lmn} would be labeled by three integer indices and the same procedure would lead to a T^4 temperature dependence for a large container.

III. NORMAL MODE STRUCTURE AND CASIMIR FORCES

The Stefan-Boltzmann law in (7) gives the temperature dependence of the total thermal energy but provides no information regarding the spectrum of thermal radiation. Now in obtaining Eq.(7), we took the limit of a large box L and so replaced the sum over normal modes by an integral. However, by going to the continuum limit, we lost the information which might be available in the discrete spectrum of the normal modes. It was Casimir who saw the possibility of new forces and energies linked to this discreteness of the classical normal mode structure. The most famous example of such forces is the original Casimir calculation[6] of the force between conducting parallel plates arising from electromagnetic zero-point radiation. Casimir worked specifically with zero-point fields; however, the idea is not limited to zero-point radiation. Any spectrum of random classical radiation will lead to Casimir energies associated with the discrete classical normal mode structure of a container.[13] Indeed, every thermodynamic variable (energy, entropy, free energy, force) will depend upon the normal modes structure.

It should be emphasized how totally different this classical wave situation is from the classical particle situation of ideal gas particles in a box. Thus if a box with reflecting walls is filled with ideal gas particles at temperature T, then the introduction of a thin reflecting partition does not change the system energy and does not involved any average force on the partition. In total contrast, the introduction of a conducting partition into a conducting-walled box of thermal radiation leads to a change in the normal mode structure and hence both to position-dependent energy changes (Casimir energies) and to average forces on the partition (Casimir forces). These Casimir energies and forces will depend upon the precise spectrum of random radiation and upon the precise location of the partition. In this article we note that the Planck spectrum for thermal radiation equilibrium can be obtained from a natural maximum-entropy principle for the Casimir energy changes associated with the placement of partitions in boxes of radiation.

IV. CHANGE IN CASIMIR ENERGY DUE TO A PARTITION

We now consider a one-dimensional box of length L and calculate the change of radiation energy $\Delta U(x, L, T)$ with position x for a partition which is located a distance x from the left-hand end of the box, $0 \leq x \leq L$. The energy of each normal mode of frequency ω_n is given by $\mathcal{U}(\omega_n, T)$. The partition changes the normal mode frequencies and so produces a position-dependent energy change $\Delta U(x, L, T)$ which is a Casimir energy. We will calculate the Casimir energy $\Delta U(x, L, T)$ as the change in the system energy when the partition is placed a distance x from the left-hand wall compared to when the partition is placed at $x = L/2$ in the middle of the box,

$$\Delta U(x, L, T) = \{U(x, T) + U(L - x), T\} - \{U(L/2, T) + U(L/2, T)\}$$

$$= \left\{\Sigma_{n=1}^{\infty}\mathcal{U}\left(\frac{cn\pi}{x}, T\right) + \Sigma_{n=1}^{\infty}\mathcal{U}\left(\frac{cn\pi}{L-x}, T\right)\right\} - 2\Sigma_{n=1}^{\infty}\mathcal{U}\left(\frac{cn\pi}{L/2}, T\right) \tag{8}$$

V. CASIMIR ENERGY FOR THE ZERO-POINT SPECTRUM

Equation (8) for the Casimir energy $\Delta U(x, L, T)$ of a box has been expressed as a sum over the total energy of each normal mode. Before we can discuss a maximum entropy principle involving this energy, we must know that it is well-defined. We have already noted that the sum over the thermal energy $\mathcal{U}_T(\omega, T)$ of the modes represents the total thermal energy U_T and is finite, while the sum including the zero-point energy $\mathcal{U}_{zp}(\omega)$ is divergent. However, the Casimir energy $\Delta U(x, L, T)$ in (8) can be defined as a limit and is finite. We recall that, in contrast to an ideal system, any physical wave system (such as a string with clamped ends or else electromagnetic fields in a region bounded by good conductors) will not enforce the normal mode structure at very high frequencies (short wavelengths). Thus it is natural to introduce a smooth cut-off $\exp(-\Lambda\omega/c)$ related to frequency $\omega = ck$

$$U(L, T, \Lambda) = \Sigma_{n=1}^{\infty}\mathcal{U}(\omega_n, T)\exp(-\Lambda\omega_n/c) \tag{9}$$

Next we carry out the subtractions corresponding to (8) to obtain the Casimir energy, $\Delta U(x, L, T, \Lambda)$, and then allow the no-cut-off limit $\Lambda \to 0$. Although here we will work with an exponential cut-off because it is easy to sum the geometric series, the result is very general; any smooth cut-off function dependent on frequency alone will give the same result[14].

In this fashion, we can calculate the Casimir energy for the zero-point radiation spectrum in (5),

$$\Delta U_{zp}(x, L) = lim_{\Lambda\to 0}\left\{\Sigma_{n=1}^{\infty}\frac{1}{2}\frac{cn\pi}{x}\exp\left(-\Lambda\frac{n\pi}{x}\right) + \right.$$

$$\left. + \Sigma_{n=1}^{\infty}\frac{1}{2}\frac{cn\pi}{L-x}\exp\left(-\Lambda\frac{n\pi}{L-x}\right) - 2\Sigma_{n=1}^{\infty}\frac{1}{2}\frac{cn\pi}{L/2}\exp\left(-\Lambda\frac{n\pi}{L/2}\right)\right\}$$

$$= lim_{\Lambda\to 0}\left\{-\frac{c}{2}\frac{\partial}{\partial\Lambda}\left[\frac{1}{\exp[\Lambda\pi/x] - 1} + \frac{1}{\exp[\Lambda\pi/(L-x)] - 1} - 2\frac{1}{\exp[\Lambda\pi/(L/2)] - 1}\right]\right\}$$

$$= lim_{\Lambda\to 0}\left\{\left[\frac{cx}{2\Lambda^2\pi} - \frac{c\pi}{24x} + \bigcirc(\Lambda)\right] + \left[\frac{c(L-x)}{2\Lambda^2\pi} - \frac{c\pi}{24(L-x)} + \bigcirc(\Lambda)\right] - \right.$$

$$-2\left[\frac{c(L/2)}{2\Lambda^2\pi}-\frac{c\pi}{24(L/2)}+\bigcirc(\Lambda)\right]\Bigg\} = -\frac{c\pi}{24}\left(\frac{1}{x}+\frac{1}{L-x}-\frac{2}{L/2}\right) \tag{10}$$

Thus we obtain the change in zero-point energy associated with the position x of the partition,

$$\Delta U_{zp}(x,L) = -\frac{c\pi}{24}\left(\frac{1}{x}+\frac{1}{L-x}-\frac{2}{L/2}\right) \tag{11}$$

The total Casimir energy at finite temperature T then involves

$$\Delta U(x,L,T) = \Delta U_T(x,L,T) + \Delta U_{zp}(x,L) \tag{12}$$

where ΔU, ΔU_T, ΔU_{zp} are formed from the respective mode energies $\mathcal{U}$, $\mathcal{U}_T$, and $\mathcal{U}_{zp}$. From the result (11) for zero-point energy, we see that $\Delta U(x,L,T)$ is finite for any spectrum $\mathcal{U}_T$ of thermal radiation which has finite total energy U_T.

VI. MAXIMUM ENTROPY PRINCIPLE FOR THERMAL RADIATION

Suppose now that we consider a collection of conducting-walled boxes of length L which differ only in the placement of the partition. Our ideas of uniformity suggest that the collection should have the partitions distributed uniformly in x along the open interval $(0,L)$. If each of these boxes contained thermal radiation at the same temperature T, then they would still differ in their total energies because of the presence of the partitions at different locations and the associated difference in Casimir energies. We notice how strikingly different this is from the situation which is usually described in thermodynamics texts where we are dealing with ideal gas particles in a box. For ideal gas particles in a box, the insertion of a thin partition into the equilibrium situation would not change the total energy or the entropy for the box; each box would have the same energy. Yet in our situation of thermal radiation, the boxes each have the same temperature yet each has a different energy. The natural situation of maximum entropy corresponds to maximum uniformity of energy among the boxes.

In order to turn this natural-maximum-entropy idea into a numerical criterion, we must turn back to Wien's displacement theorem to note the allowed functional form for $\mathcal{U}_T(\omega,T)$ and to fix the connection between the possible radiation spectra and temperature. We have already indicated that the thermodynamics associated with the Wien displacement theorem gives thermal radiation $\mathcal{U}\rightarrow\mathcal{U}_{RJ}(\omega) = T \quad \text{for} \quad \omega/T << 1$. Thus the temperature of the random radiation fixes the low-frequency limit of $\mathcal{U}_T(\omega,T)$. Furthermore, the thermal energy of each normal mode must be non-negative $\mathcal{U}_T(\omega,T)\succeq 0$, and the total thermal energy must be finite. These criteria can be met by any distribution of normal mode thermal energies

$$\mathcal{U}_T(\omega,T) = T\,f(\omega/T) \tag{13}$$

where f is an arbitrary function satisfying

$$f(0)=1, \quad f(x)\succeq 0, \quad \int_0^\infty dx\, f(x) < \infty \tag{14}$$

If we calculate the Casimir energy $\Delta U(x,L,T)$ in (8) using (11) and (12) with any function f satisfying the criteria of (14), then the departure I from a uniform energy among the partitioned boxes is given by

$$I = \sum_i |\Delta U(x_i, L, T)| \tag{15}$$

where the sum is over the uniformly-distributed partition locations x_i. Since the Casimir energy vanishes for the partition at $x = L/2$ and is symmetric about this point, this sum allows an immediate conversion to an equivalent integral

$$I = \int_{x=\delta}^{x=L/2} dx \; |\Delta U(x, L, T)| \tag{16}$$

where δ is a small cut-off distance which is much less than any other length in the situation, $0 < \delta << min(L, c/T)$. The need for such a cut-off arises because of the divergence of the zero-point Casimir energy at small distances. The natural maximum-entropy principle states that nature will choose the function $f(x)$ satisfying the criteria in (14) which makes the integral I in(16) a minimum.[15]

VII. CASIMIR ENERGIES FOR VARIOUS RADIATION SPECTRA

In one spatial dimension, it is quick to evaluate the Casimir energies for various monotonic spectral functions $\mathcal{U}(\omega, T)$ on a home computer. One separates out the divergent zero-point energy contribution corresponding to (11) and then evaluates the thermal contribution to the Casimir energy for any assumed thermal spectrum $\mathcal{U}_T(\omega, T) = T f(\omega/T)$ meeting the criteria of (14). The total Casimir energy $\Delta U(x, L, T)$ is the sum of the thermal and zero-point contributions.

For all spectra $\mathcal{U}_T(\omega, T)$ satisfying the required conditions (14), we can calculate the test integral given in Eq.(16). The spectrum providing the smallest value for the integral appears to be the Planck spectrum with zero-point radiation

$$\mathcal{U}_{Pzp}(\omega, T) = \frac{1}{2}\omega \coth\left(\frac{1}{2}\frac{\omega}{T}\right) = \frac{\omega}{\exp(\omega/T) - 1} + \frac{1}{2}\omega \tag{17}$$

Indeed, we may use the Planck form (or other functional forms) in a variational calculation to obtain the parameters which give the smallest value to the test integral for the given functional form. Thus the Planck form for the thermal part of the radiation at frequency ω can be written as

$$\mathcal{U}_{PT}(\omega, T) = \mathcal{U}_P(\omega, T) - \frac{1}{2}\omega = \frac{\omega}{\exp(\omega/T) - 1} \tag{18}$$

We can introduce parameters C_1 and C_2 into a generalization of this form giving an energy spectrum including zero-point energy as

$$\mathcal{U}_{C_1 C_2}(\omega, T) = \frac{C_1 \omega \exp[-C_2(\omega/T)]}{1 - \exp[-C_1(\omega/T)]} + (1/2)\omega \tag{19}$$

For all positive parameters C_1 and C_2, this spectrum goes over to energy equipartition in the limit $\omega \to 0$ and goes over to zero-point energy at high frequency while giving finite total thermal radiation energy. Accordingly we can search for the the values of C_1 and C_2 which make the test integral (16) a minimum. Numerical calculation shows that the minimum value for the test integral is achieved when $C_1 = C_2 = 1$, corresponding to exactly the Planck spectrum (17).

Indeed, of all the functional forms tested numerically, the Planck spectrum gave the smallest value of the test integral. We conjecture that analytic calculation[16] would show that this spectrum provides the minimum for this integral, and hence in this sense provides the smallest Casimir energies and greatest uniformity in the presence of zero-point radiation.

VIII. CASIMIR ENERGY FOR THE RAYLEIGH-JEANS SPECTRUM

In the current textbook accounts of blackbody radiation, zero-point radiation is not considered, and the Rayleigh-Jeans spectrum is said to be the spectrum predicted by classical physics. It therefore seems of interest to calculate the Casimir energies associated with the Rayleigh-Jeans spectrum in (5). This spectrum is simple enough to allow analytic calculation of the Casimir energies. We again make use of a high frequency cut-off just as in the case of the zero-point spectrum, and calculate

$$\Delta U_{RJ}(x, L, T) =$$

$$= lim_{\Lambda\to 0}\left\{\Sigma_{n=1}^{\infty} T\exp\left(-\Lambda\frac{n\pi}{x}\right) + \Sigma_{n=1}^{\infty} T\exp\left(-\Lambda\frac{n\pi}{L-x}\right) - 2\Sigma_{n=1}^{\infty} T\exp\left(-\Lambda\frac{n\pi}{L/2}\right)\right\}$$

$$= lim_{\Lambda\to 0}\left\{\frac{T}{\exp[\Lambda\pi/x]-1} + \frac{T}{\exp[\Lambda\pi/(L-x)]-1} - 2\frac{T}{\exp[\Lambda\pi/(L/2)]-1}\right\}$$

$$= lim_{\Lambda\to 0}\left\{T\left[\frac{x}{\Lambda\pi} - \frac{1}{2} + \frac{\pi\Lambda}{12x} - ...\right] + T\left[\frac{L-x}{\Lambda\pi} - \frac{1}{2} + \frac{\pi\Lambda}{12(L-x)} - ...\right] + \right.$$

$$\left. -2T\left[\frac{L/2}{\Lambda\pi} - \frac{1}{2} + \frac{\pi\Lambda}{12(L/2)} - ...\right]\right\} = 0 \tag{20}$$

Thus we find that the Rayleigh-Jeans spectrum gives no Casimir energy changes at all. Indeed, the Rayleigh-Jeans spectrum is the unique spectrum which produces no Casimir energy changes associated with the placement of the Casimir partition, $\Delta U_{RJ}(x, L, T) = 0$.[17]

IX. 'ULTRA-VIOLET CATASTROPHE' WITHOUT ZERO-POINT RADIATION

We should emphasize that our maximum entropy principle indeed requires the presence of the zero-point radiation energy. If no zero-point energy were present, then we would still require that the thermal spectrum give energy equipartition at low frequency and go to zero at high frequency so as to give a finite energy density for thermal radiation. For this case, the thermal energy would be the total energy used in (16). However, there would be no natural high-frequency limit. If we tried a smooth spectrum such as that suggested by Rayleigh $\mathcal{U}_{RT}(\omega, T) = T\exp[-C(\omega/T)]$ with an adjustable parameter C but without zero-point energy, then we would find that the test integral given in Eq.(16) decreases as the parameter C decreases, bringing the spectrum ever closer to the Rayleigh-Jeans spectrum, in which limit the integral vanishes $I = 0$ and there are no Casimir energy changes. The absence of any natural cut-off frequency represents behavior reminiscent of the "ultraviolet catastrophe" emphasized by Einstein and named by Ehrenfest in 1911. What prevents the catastrophic shift of thermal radiation to ever-higher frequencies is precisely the presence of zero-point radiation.

X. CONCLUDING SUMMARY

In this analysis, we have treated the thermodynamics of waves in one spatial dimension. However, the ideas can be carried over to electromagnetic waves in three spatial dimensions. Although the Wien displacement theorem reflects the information from adiabatic energy changes of the known harmonic oscillator Lagrangian for the electromagnetic modes of thermal radiation, the entropy associated with each mode is undetermined. Traditional classical physics does not find it possible to recognize a situation of natural maximum uniformity, of maximum entropy. However, the use of Casimir energies, which connect different radiation spectra to different total radiation energies in a partitioned box, allows one to find a situation of natural maximum entropy. In the absence of zero-point radiation, the entropy principle recovers only the Rayleigh-Jeans spectrum. In the presence of zero-point radiation, numerical calculation indicates that the spectrum of maximum entropy is the Planck spectrum.

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[1] See, for example, R. Eisberg and R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles 2nd ed.* (Wiley, New York 1985), Chapter 1.

[2] See, for example, M. Planck, *The Theory of Heat Radiation* (Dover, New York 1959), pp. 61-63, or R. Becker and G. Leibfried, *Theory of Heat 2nd ed.* (Springer, New York 1967), pp. 16-17, or P.M. Morse, *Thermal Physics 2nd ed* (Benjamin/Cummings, Reading, MA 1969), pp. 78-79.

[3] See, for example, M. Planck in reference 1, pp. 72-83, or F. K. Richtmyer, E. H. Kennard, and T. Lauritsen, *Introduction to Modern Physics* (McGraw-Hill, New York 1955), pp. 113-118, or B. H. Lavenda, *Statistical Physics: a Probabilistic Approach* (Wiley, New York 1991), pp. 67-69. A very different derivation is presented by T. H. Boyer, "Thermodynamics of the harmonic oscillator: Wien's displacement law and the Planck spectrum," submitted for publication.

[4] Physicists today usually regard zero-point radiation as a "quantum" phenomenon. However, zero-point radiation can also be regarded as classical random radiation, just as thermal radiation was regarded as classical random radiation before 1900.

[5] M. J. Sparnaay, "Measurement of the attractive forces between flat plates," Physica **24**, 751-764 (1958); S. K. Lamoreaux, "Demonstration of the Casimir force in the 0.6 to 6μm range," Phys. Rev. Lett. **78**, 5-8 (1997), **81**, 5475-5476 (1998); U. Mohideen, "Precision measurement of the Casimir force from 0.1 to 0.9 μm," Phys. Rev. Lett. **81**, 4549-4552 (1998); and H. B. Chan, V. A. Aksyuk, R. N. Kleiman, D. J. Bishop, and F. Capasso, "Quantum mechanical

actuation of microelectomechanical systems by the Casimir force," Science **291**, 1941-1944 (2001).
[6] H. B. G. Casimir, Proc. Kon. Ned. Akad. Wetenschap. **51**, 793 (1948).
[7] In this article we have discussed the case of waves in one spatial dimension. However, the same thermodynamic analysis applies immediately in three dimensions. The behavior of Casimir forces within a three-dimensional rectangular conducting box with a conducting partition can be shown numerically to repeat the same sort of behavior as found in the one-dimensional case. Indeed, related calculations were done decades ago in the three-dimensional calculations of M. Fierz, "Zur Anziehung leitender Ebenen im Vacuum, "Helvetica Physica Acta **33**, 855-858 (1960), and of T. H. Boyer, "Some Aspects of Quantum Electromagnetic Zero-Point Energy and Retarded Dispersion Forces," Harvard doctoral thesis 1968 (unpublished), particularly Fig. 4.
[8] See, for example, E. A. Power, *Introductory Quantum Electrodynamics* (American Elsevier, NY 1964), pp. 18-22.
[9] Here $\mathcal{U}$ is written in terms of the thermodynamic potential $\phi(\omega/T)$ used by C. Garrod, *Statistical Mechanics and Thermodynamics* (Oxford, New York 1995), p. 128. See the references in 3.
[10] See the discussion of natural units by C. Garrod, reference 9, p. 120. The choice $\hbar = 1$ is familiar to particle physicists. The measurement of temperature in energy units is familiar in thermodynamics where our choice corresponds to the use of what is usually termed τ instead of T.
[11] See, for example, Boyer in reference 3.
[12] It is amusing to carry out Boltzmann's derivation for the one-dimensional case. We assume that the thermal energy and entropy of our waves in a very large one-dimensional box of length L satisfy $U_T(T,L) = L\,u_T(T)$, and $S(T,L) = L\,s(T)$ where the densities are functions of temperature alone. For a normally incident plane wave, we expect a pressure $p = \mathcal{E}/V$ rather than $p = (1/3)\mathcal{E}/V$. Multiplying by the area of the walls, the force on the bounding partition corresponds to $X = u$ where u is the energy per unit length. These are electromagnetic results which involve no thermodynamics. Now substituting into $TdS(T,L) = dU_T(T,L) + X_T dL$ and separating differentials on both sides, we have $s = 2u_T/T$ and $ds/dT = (1/T)(du_T/dT)$. Differentiating the equation for s with respect to temperature and substituting into the second, we find a differential equation with solution $u_T = \alpha T^2$ and so $s = 2\alpha T$ where α is an unknown constant.
[13] H. B. G. Casimir, in reference 6, gives the force per unit area due to electromagnetic zero-point radiation. The Rayleigh-Jeans spectrum gives a different force per unit area, $F/A = -\zeta(3)k_BT/(4\pi x^3)$. See, for example, T. H. Boyer, "Temperature dependence of Van der Waals forces in classical electrodynamics with classical electromagnetic zero-point radiation," Phys. Rev. A **11**, 1650-1663 (1975).
[14] See for example, G. H. Hardy, *Divergent Series* (Oxford University Press, London, 1956).
[15] We notice that thermodynamics actually requires that $\mathcal{U}(T,\omega)$ be a monotonically increasing function of frequency as it goes from the low frequency limit $\mathcal{U}(T,\omega) = T$ to the high-frequency limit $\mathcal{U}(T,\omega) = (1/2)\omega$. This already puts additional restrictions on the monotonically decreasing functions $f(\omega/T)$. However, we find that even monotonically decreasing functions $f(\omega/T)$ which satisfy the limits in (14), as well as giving monotonic functions $\mathcal{U}(T,\omega) = Tf(\omega/T)+(1/2)\omega$, still do not necessarily lead to monotonic Casimir energy changes $\Delta U(x,L,T)$ with partition position x. Such functions are excluded by fundamental thermo-

dynamic ideas. However, such thermodynamic restrictions are all subsumed by the maximum-entropy principle.

[16] It is curious and perhaps significant that the Euler-Maclaurin expansion which enters Casimir calculations involves the same Bernoulli numbers as appear in the coefficients of the hyperbolic tangent function. See, for example, R. P. Boas and C. Stutz, "Estimating sums with integrals," Am. J. Phys. **39**, 745 (1971) and M. Abramowitz and J. Stegun, eds., *Handbook of Mathematical Functions* (Dover, New York, 1965), pp. 804 and 806.

[17] There are, however, Casimir forces and changes in Helmholtz free energy. One also finds interesting temperature-independent entropy changes with partition position $\Delta S_{RJ}(x, L, T) = (1/2) |\ln[x/(L-x)]|$. This seems reminiscent of temperature-independent changes associated with the mixing entropy of ideal gas particles. Similar changes have been noted in quantum field theory by J. C. da Silva, A. Matos Neto, H. Q. Placido, M. Revzen, and A. E. Santan, "Casimir effect for conducting and permeable plates at finite temperature," Physica A **292**, 411-421 (2001).